

*Scientific Solutions*

**HAVE RISKS ASSOCIATED WITH THE PRESENCE  
OF SYNTHETIC ORGANIC CONTAMINANTS IN  
LAND-APPLIED SEWAGE SLUDGES BEEN  
ADEQUATELY ASSESSED?**

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**ABSTRACT**

Land application has become the dominant means for sewage sludge disposal in the United States. In 1993, the EPA concluded that synthetic organics therein posed an insignificant risk, based on the results of the 1988 National Sewage Sludge Survey, the view that most persistent organics are no longer in commerce and that industrial pretreatment further reduces their release to municipal treatment plants. However, we detected high concentrations of several problematic compounds in biosolids that were overlooked in the risk assessment, including persistent, bioaccumulative polybrominated diphenyl ethers and estrogenic nonylphenols. These results and other findings call into question the assessment's certainty.

Application of sewage sludge on agricultural, public, and reclaimed lands has become the dominant means for its disposal in the United States. While wastewater contaminants concentrate in sludge, a 1993 U.S. EPA risk assessment concluded that land application of sludge-associated synthetic organics does not pose significant risks and thus need not be regulated. EPA based this on a 1988 analytical survey that failed to detect significant burdens of targeted organics in sludge, the view that persistent organics of concern have been removed from commerce and that industrial pretreatment limits release of problematic organics to treatment plants. However, we detected high concentrations of polybrominated diphenyl ethers and nonylphenols, recently recognized as contaminants of concern, in sludges from several U.S. states. These pollutants were not considered

in the EPA risk assessment. Potential additive effects of the myriad of contaminants in sludge were also not evaluated. These results call into question the certainty of the assessment conclusions.

Effective treatment of wastewaters is an onerous task due to the tremendous volumes generated and the diversity of chemicals contained therein. It has been estimated that as many as 100,000 chemicals are in commerce and thus can potentially enter wastewater [1]. In addition, about a thousand new compounds are introduced annually, making static environmental regulations untenable. Degradative processes are essential elements of the treatment process, but often are incomplete, generating additional intermediates of toxicological concern. While the goal of the treatment process is to produce an aqueous effluent free of short- or long-term environmental or health effects, an additional product is a solid residue. This sludge is formed by flocculation of dissolved and suspended materials originally present in the wastewater. Hydrophobic chemicals preferentially sorb to the particulates and associated organic matter and are then removed from the water column by settling. Thus, sludge is enriched not only in nutrients and organic carbon, but also pollutants.

Approximately 6.9 million dry tons of sewage sludge were generated in the United States in 1998 [2]. The amount is expected to increase as wastewater treatment improves and the population served grows. Disposal of this material is a significant issue. Sludge may be incinerated. However, facilities required are expensive and must be properly engineered and maintained to minimize production of by-products, such as chlorinated dioxins. Landfilling of sludge has been portrayed as a waste of disposal capacity and valuable real estate. While the number of landfills has decreased from 8,000 to 2,300 from 1988 to 1999, total capacity has remained relatively constant [3]. If all U.S. sludge was landfilled, it would constitute only about 5 percent of the total dry weight of solid waste disposed of in that manner. A third option, ocean disposal, fell into disfavor largely due to incidents involving debris on northeastern U.S. shorelines and related beach closings. Sanctioned ocean disposal of sludge ended in 1992 as a result of the Ocean Dumping Act. Factors favoring land application of sewage sludge include reutilization of the nutrients contained therein and enhancement of soil porosity and organic content. Land application is often the most economic means of sludge disposal compared to the alternatives, at least for the generator. As a result it has become the dominant disposal mechanism in the United States, encompassing more than half of the wastewater treatment plant (WWTP) sludge produced. After generation at the WWTP, sewage sludge typically is further processed or "stabilized" to reduce its water and pathogen content. The term "biosolids" has been coined for this product. Biosolids are subsequently given away or sold at low cost to farmers, the general public or others.

However, land application of sludge may present health risks, due to the presence of pathogens, toxic metals, and organic pollutants. Pathogens may

remain viable in sludge to varying degrees as a function of the stabilization technique employed. Toxic metals do not breakdown in the treatment process or in the environment. As a consequence, they can build up in soil upon repeated application and thus are regulated by the EPA Part 503 regulations [4]. Nonetheless, limitations on metal burdens in U.S. biosolids are among the most lenient in the world [5]. No U.S. regulations exist limiting organic pollutant burdens. The diversity of organics in sludge is tremendous. While some are easily degraded, others are persistent. Nonetheless, the EPA concluded in its risk assessment that organics present in sludge present no significant risks as a result of land application. It is instructive to examine this exercise in more detail. The foundation of risk assessment is hazard identification, requiring the development of a complete list of the contaminants of concern [6]. This is somewhat problematic for a material as complex and variable as sludge.

Much of the biosolids contaminant concentration data used in the initial risk assessment effort was obtained from EPA's *Fate of Priority Pollutants in Publicly Owned Treatment Works*, the so-called "40 Cities Study" published in 1982 [7]. Based on this survey and existing data on pollutant toxicities, a list of 200 potential metals and synthetic organics of concern was initially generated by EPA in 1984 [6]. These target compounds represent less than 1 percent of those in commerce. The list was pared to about 50, including 30 individual organic pollutants or groups of compounds (e.g., PCBs) by expert panels. Hazard indices were then determined by comparing expected exposure to a given contaminant via most likely routes (e.g., ingestion of soil) to established human health or other accepted regulatory criteria. Next, hazard rankings were developed based solely on exposure to a contaminant via biosolids alone. Ten organics met or exceeded an index value of 1.0 (exposure/toxicity ratio) in this evaluation. Five additional compounds that had been deleted earlier were later re-added to these ten and subjected to additional scrutiny.

At this juncture of the review process, circa 1989, it was felt that the data from the 1982 "40 Cities Study" was outdated. More stringent industrial pretreatment regulations had taken effect, resulting in generally lower pollutant burdens in influents. Wastewater treatment processes and analytical techniques had also improved. Further, some of the plants examined in the 1982 study had significant industrial input and thus were not representative of the population of WWTPs from which biosolids were typically derived. Finally, the sludges analyzed previously were taken from several stages in the treatment process. Thus they were not representative of the final processed sludge that ultimately serves as the source for the land-applied material. In 1988, the National Sewage Sludge Survey (NSSS) was initiated. It involved 180 facilities and 412 chemicals, chosen in part on the availability of analytical reference standards [6]. This study ultimately concluded that organic pollutant levels in sludge were low. In the end, EPA chose to exclude all organic pollutants from the Part 503 regulations based on the following arguments: 1) persistent pollutants of concern have been restricted or

banned from use or manufacture in the United States; 2) the NSSS showed that organic pollutants were not present in sludge at “significant frequencies of detection”; and 3) pollutant concentrations in sludge were less than those determined to be of concern in the risk assessment [6]. Section 405 of the Clean Water Act required EPA to consider a second round of biosolid contaminants for possible regulation. However, a new sludge analysis survey was not conducted and EPA is currently only considering setting limits for chlorinated dioxin-like compounds [8].

Risk assessment is a logical framework for policy development. However, its validity depends on the availability and incorporation of complete data. Recognizing this difficulty and associated time lags, other countries have occasionally used the precautionary principle. Detrimental health effects are a function of all of the chemicals to which organisms are exposed, not just those on regulatory lists or for which detection is convenient using available technology or analytical standards. Most risk assessments also consider only the “worst-case” single chemical exposure, not simultaneous exposure pathways or coincident exposure to multiple chemicals. Recently, it has been observed that simultaneous exposure to several endocrine-disrupting chemicals was capable of generating an observable effect, even though each was present below its respective effects threshold [9]. Some proponents have used the paucity of demonstrated, well-documented detrimental impacts of sludge land application as a rationale not to fill gaps in the database critical to the risk assessment. This is unsatisfying and undermines the contention of the same proponents that risk assessment is superior to alternative strategies as it is based on “sound science.” It also transfers the burden of proof from those who benefit from the action to those who might be damaged by an erroneous conclusion as to safety. Regardless, consideration of our past track record of recognizing deleterious effects in the field due to synthetic chemicals is not encouraging. For example, diethylstilbestrol, PCBs, DDT, and chlorofluorocarbons were all assumed to be harmless after initial testing and were used for years before their consequences were fully realized.

One of the conclusions of the EPA risk assessment is that organic pollutants are not present in land-applied sludges at concentrations hazardous to living resources. Obviously, a precondition to this is that the assessor possesses complete data on the identities and quantities of the chemicals actually in sludge. We present information below that suggests this was not the case.

### **BROMINATED FLAME RETARDANTS (BFRs)**

BFRs are current-use synthetic organic compounds. There are several different BFR chemicals in commerce, but here we restrict our attention to the polybrominated diphenyl ethers (PBDEs) due to recent recognition of their importance as chemicals of environmental and human health concern. PBDEs are used

in increasing amounts in North America. They are chemically related to PCBs and polybrominated biphenyls (PBBs) and replaced them in some similar applications. PBDE demand in North America, 33,965 metric tons in 1999, represented more than 50 percent of the world's entire consumption [10]. Three formulations, mixtures of PBDE congeners possessing related degrees of bromination, are in commercial production: Deca-BDE (used primarily in thermoplastics and as a back-coating on textiles), Octa-BDE (mostly in thermoplastics and electrical wire coatings), and Penta-BDE (predominantly in polyurethane foam, in turn used in furniture and padding). These products constitute 82 percent, 5.7 percent, and 12.7 percent respectively of the global PBDE market. PBDEs are added to polymers during their formation, but do not covalently bond to them. Thus a small percentage may potentially migrate from the polymer over time. Release to the environment may be greatly accelerated if the polymer itself degrades, as in the case of polyurethane foam [11]. All three PBDE mixtures appear to be environmentally persistent. Penta-BDE is likely the most problematic from a bioaccumulation and toxicological standpoint. Bioconcentration factors for its constituents are comparable to or exceed those of PCBs [12]. About 98 percent of the global demand for Penta-BDE now resides in North America, fostered by well-intended legislation to mitigate the role furniture plays in fires. The Octa- and Deca-BDE mixtures appear to present less of a hazard due to their lower bioavailability and mobility, a result of their extraordinarily low water solubilities and volatilities [13].

Components of the Penta-BDE mixture have now been detected in organisms from even remote areas, for example, marine mammals from the Canadian Arctic [14]. The expected route is via atmospheric transport. PBDEs have been detected in air from both urban and rural areas [15]. In 2001 we reported detectable concentrations ( $> 5 \text{ ug/kg}$  lipid basis) in the edible flesh of nearly 90 percent of the fish samples examined from Virginia waters [16]. Consumption of contaminated fish is believed to be a mechanism for human exposure [17]. PBDEs have also been detected in humans. Until recently, when Penta-PBDE use dropped in Europe, levels in human breast milk in Swedish women were reported to be doubling every five years [18]. The increasing PBDE concentrations were sufficient to trigger European Union action to ban Penta-BDE, effective in 2003. Further assessment of the hazards of Deca-BDE and Octa-BDE mixtures are ongoing. In 2002, it was reported that breast milk from North American women showed a similar increasing trend in PBDE levels [18]. However, concentrations appear to be 40-times higher, consistent with the greater Penta-BDE usage here. Some have suggested that environmental PBDE levels may be driven by decomposition of the more commonly used Deca-BDE product [19]. However, evidence of extensive debromination to Penta-BDE-like congeners in the environment is lacking to date.

Our understanding of the toxicological potential of PBDEs is incomplete and studies to further elucidate their effects are underway. PBDEs appear to have low

acute toxicity, but chronic exposure or exposure during development may compromise the endocrine and nervous systems [20, 21]. This is particularly troubling in light of the 2002 report that PBDEs in infant serum were higher than those in other age groups [22]. PBDEs, and even more so their metabolites, are structurally similar to the thyroid hormone thyroxine (T4) (Figure 1). Some have been observed to displace T4 from the plasma transport protein transthyretin *in-vitro* [23]. Little information on effects of PBDEs on humans exists. However, the structurally related PBBs have been associated with precocious pubertal events in exposed girls [24].

### ALKYLPHENOL POLYETHOXYLATES (APEOs)

APEOs are predominantly used as surfactants in heavy-duty detergents. The nonylphenol polyethoxylates (NPEOs) constitute about 80 percent of the APEO market, with octylphenol analogs (OPEO) constituting the bulk of the remainder [25]. Interestingly, NPEOs have also been used as human spermicides. In 2000,

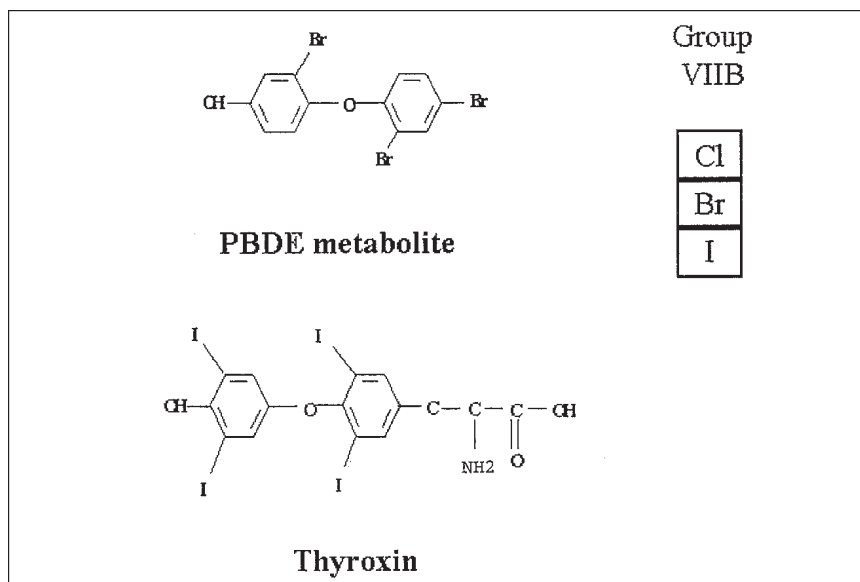


Figure 1. PBDE metabolites bear a striking resemblance to the thyroid hormone thyroxine and can compete with it for binding sites on the transport protein transthyretin. The halogens (Cl, Br and I) all belong in Group VIIB of the periodic chart. However, Br is more similar to I, the latter contained in thyroxine, than Cl. PBDEs are identical to PBBs except for the presence of the ether linkage in the former.

U.S. demand for NPs, mainly as NPEO precursors, was 109 million kg [26]. Growth of U.S. demand for NP has been about 2 percent per year since 1996 and NPEO exports doubled to 22 million kg from 1999 to 2000. In contrast, several European countries, e.g., Norway, Switzerland, and Denmark, have reduced their use of APEOs in light of the detection of part-per-million NP concentrations in aquatic sediments and sludges and elucidation of their toxic and endocrine-disruptive properties. NPs are acutely toxic to some aquatic organisms ( $< 10 \mu\text{g/l}$  water column or  $315 \text{ mg/kg}$  in sediments) [27, 28] and have been linked to impacts on some endocrine-related processes at less than  $10 \mu\text{g/L}$  [29]. Less is known regarding effects in terrestrial systems.

APEOs themselves have relatively low toxicities and generally are believed to degrade in the environment in the presence of oxygen. However, a fraction of the APEOs may be incompletely degraded to the corresponding alkylphenols (APs: mostly NPs and OP), especially under low oxygen conditions, such as those present in some WWTPs [30]. APs are moderately hydrophobic and partition preferentially to particulates and thus accumulate in sediments and sewage sludge. In testament to this pattern, we observed NP burdens of  $54,400 \mu\text{g/kg}$  in York River surficial sediments, near a WWTP that ceased operation more than 20 years previously [31]. A half-life in excess of 60 years was calculated for APEOs in cold, anoxic sediments from British Columbia [32]. Obviously, consideration of the environment to which pollutants are released must be factored in when estimating their persistence.

Uptake and retention of NPs and OP by organisms may explain their reported greater estrogenicity *in vivo* compared to *in vitro* assays [33]. In the field, reproductive disturbances in wild fish populations have been observed near WWTP outfalls, including intersexuality, vitellogenesis, and decreased gonadosomatic index (ratio of gonadal size to body weight) [34]. In all likelihood, these impacts are a result of exposure to a combination of endocrine-disrupting chemicals. In addition, applications of NP-containing insecticides on Canadian forests have been implicated in declines of Atlantic salmon returns, possibly due to impacts on developing smolt [35]. These data demonstrate that exposure in the field to estrogenic chemicals has deleterious consequences to wildlife.

### **SURVEY OF PBDEs AND APs IN U.S. BIOSOLIDS**

We examined sewage sludges generated by WWTPs located in six different U.S. states for APs, PBDEs, and related compounds (Table 1). All biosolids had been subjected to additional stabilization procedures in preparation for land application, including: liming, composting, anaerobic digestion, and heat treatment. Samples selected included Class A (low pathogens) and Class B (application restrictions due to pathogen burdens) biosolids. Analytical procedures have been described elsewhere [36, 37]. Briefly, samples were lyophilized, surrogate standards added, extracted by enhanced solvent extraction and purified by



Table 1. Total AP, Penta-BDE, and Deca-BDE Concentrations ( $\mu\text{g/kg}$  Dry Weight Basis) in the U.S. Biosolids Examined

| Location<br>(U.S. state) <sup>a</sup> | Biosolid<br>stabilization<br>technique | Biosolid<br>class | % total<br>organic<br>carbon | Total<br>AP + NP1EOs<br>+ NP2EOs <sup>b,c</sup> | Total<br>Penta-like<br>PBDEs | Deca-<br>PBDE |
|---------------------------------------|--|-------------------|------------------------------|---|------------------------------|---------------|
| VA                                    | compost                                | A                 | 9.90                         | 6,100   | 1500                         | 308           |
| VA                                    | compost                                | A                 | 18.5                         | 176,000   | 2290                         | 1460          |
| TX                                    | compost                                | A                 | 16.1                         | 14,200  | 1290                         | 368           |
| VA                                    | lime                                   | B                 | 12.3                         | 932,000   | 1110                         | 553           |
| VA                                    | lime                                   | B                 | 24.6                         | 529,000   | 1660                         | 84.8          |
| NY/MD                                 | heat                                   | A                 | 24.9                         | 544,000   | 1500                         | 1940          |
| NJ                                    | heat                                   | A                 | 32.0                         | NA  | 2110                         | 4890          |
| CA                                    | anaerobic                              | B                 | 23.5                         | 721,000   | 1430                         | 347           |
| CA                                    | anaerobic                              | B                 | 22.2                         | 758,000   | 1100                         | 340           |
| CA                                    | anaerobic                              | B                 | 25.4                         | 925,000   | 1590                         | 450           |
| CA                                    | anaerobic                              | B                 | 20.6                         | 768,000   | 1620                         | 389           |
| CA                                    | anaerobic                              | B                 | 28.8                         | 981,000   | 2010                         | NA            |
| Mean                                  |  |                   | 21.6                         | 578,000   | 1600                         | 1010          |
| Median                                |  |                   | 22.9                         | 721,000   | 1550                         | 389           |
| Std. Dev.                             |  |                   | 6.48                         | 362,000   | 375                          | 1400          |
| CV                                    |  |                   | 30.1%                        | 62.6%   | 23.4%                        | 139%          |

<sup>a</sup>CV = coefficient of variability. <sup>b</sup>NA = analyte not determined in this sample. <sup>c</sup>Total includes NPs, OP, and the NP mono- and diethoxylates.

adsorptive and size exclusion liquid chromatography. Compounds were identified and quantified by gas chromatography (GC) with mass spectrometric (MS) and electrolytic conductivity detection in the halogen selective mode (ELCD-HSM). A major strength of modern analytical procedures is their selectivity and sensitivity. For this reason, MS in the selected ion mode (SIM) is increasingly used in environmental studies. In SIM-MS only specific ion fragments of the desired target compound(s) are monitored and recorded. Compounds not exhibiting these fragments upon ionization generate no response. This avenue provides a very specific and accurate measurement capability, even when considerable numbers/amounts of co-extracted compounds are present. The downside is that other pollutants present in the sample may be overlooked. This may explain the failure to detect the NPs and PBDEs in previous EPA sludge surveys. Figure 2 shows a chromatogram from the GC/ELCD-HSM analysis of a sludge sample. The Penta-BDE related congeners (BDE-47, 99, 100, 153 and



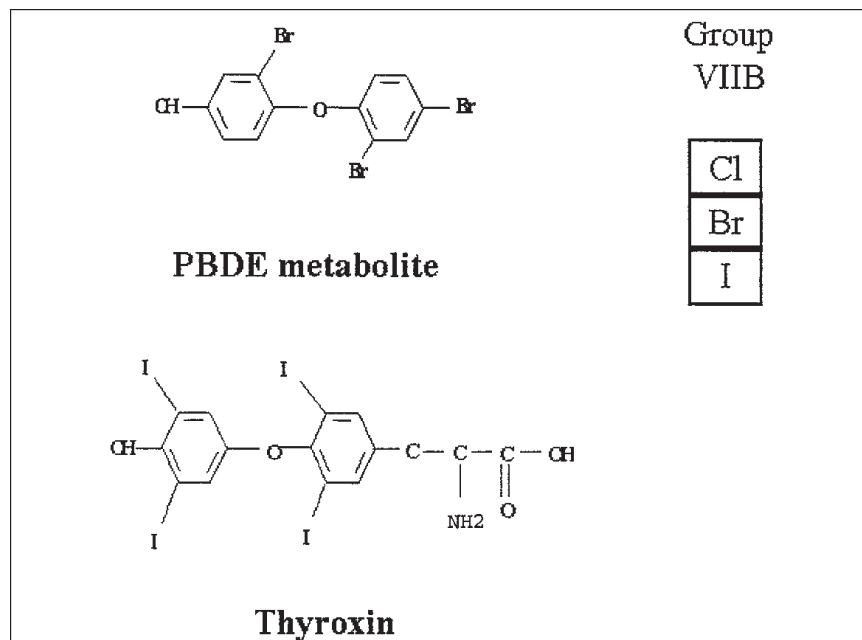


Figure 2. Chromatogram of a biosolid extract using the halogen selective ELCD. The largest peaks observed belong to the PBDEs (i.e. BDE-47 and 99), rather than to the chlorinated pollutants (e.g., PCBs and chlordanes) considered by EPA in their risk assessment. Note that the NSSS reported a detection frequency of 0 percent for chlordane. istd = internal standard added to the sample for quality control and quantification purposes.

154) are obvious here, dwarfing the PCBs (most abundant congeners: PCB-153 and 138), even though this detector is about two-fold more sensitive to chlorine than to bromine. Interestingly, the NSSS failed to detect chlordanes in any sludges. Based on this and the fact that chlordane use was banned in the United States in 1988, EPA removed them from further consideration for regulation under Part 503. However, we encountered chlordanes at easily detectable levels in modern biosolids (see Figure 2). Note that Deca-BDE (BDE-209) is not shown in Figure 2 due to its long GC retention time. A separate GC run with a shorter column is required to elute Deca-BDE due to its low volatility.

Several aspects of our PBDE sludge data merit emphasis (Table 1). First, the relative abundances of the individual congeners present closely resembled those in the commercial Penta-BDE product. This suggests that PBDE input to sludge may be derived somewhat directly from the original products they were used in, as major shifts in relative congener abundances due to differences in physical

properties, such as water solubility, had not occurred. Additionally, Penta-BDE concentrations were 10-40 times greater than those in European sludges, proportional to the greater North American demand for this product [36]. Penta-BDE levels were also remarkably consistent between sludges. This suggests these PBDEs may be derived from discarded products rather than from PBDE or polyurethane foam production facilities, as manufacturers are heterogeneously distributed in the U.S. If true, improved industrial pretreatment regulations would not affect these inputs. Penta-BDE concentrations were similar as a function of the sludge stabilization processes, not surprising considering their persistence. In contrast, Deca-BDE concentrations varied substantially between sludges, ranging from 84.8 to 4890  $\mu\text{g/kg}$  (coefficient of variability (CV): 139 percent). In contrast, total Penta-BDE concentrations ranged from 1100 to 2290  $\mu\text{g/kg}$  (CV: 23.4 percent). This may relate to Deca-BDE's predominant use in environmentally stable thermoplastics and its extremely low water solubility and volatility. In contrast, the surface of polyurethane foam can degrade into a powder when exposed to outdoor weathering. This dust, which may contain 10-30 percent by weight Penta-BDE, is easily transportable by wind and water runoff. We estimate that a single medium-sized (1 kg) seat cushion, that has been flame retarded with Penta-BDE (conservatively at 10 percent by weight), contains enough PBDE to contaminate 100,000 kg (dry weight) of biosolids to a concentration of 1000  $\mu\text{g/kg}$  by weight, comparable to the mean Penta-BDE level (1560  $\mu\text{g/kg}$ ) we observed [11].

The U.S. sludges examined also contained up to 981 mg/kg of APs (total of OP, NPs, plus the NP mono- and diethoxylates, intermediate degradates of NPEOs) (Table 1). Total NP concentrations varied as a function of the sludge stabilization process. As NPs are generated from NPEOs under anaerobic conditions, it is not surprising that the anaerobically stabilized sludges had some of the highest total NP concentrations. However, relatively high levels were present in the limed and heat-treated sludges as well. NPs are vulnerable to aerobic degradation and the composted sludges had the lowest concentrations. OP was detected in nine of the 11 biosolids and also peaked in the anaerobically digested samples, but levels were typically less than 2 percent of NP concentrations.

Total NPs concentrations in all but one U.S. sludge exceeded the 10 mg/kg Danish limit for land-applied biosolids. In recent years NP burdens in Danish sludge have decreased to an average of 4 mg/kg due to reduced NPEO usage [38]. A soil Estimated No Effects Value of 0.34 mg/kg has been recommended by Environment Canada, based on potential impacts on earthworm reproduction. Assuming a biosolid application factor of 0.003 (3 tons dry biosolid to 1 acre soil, tilled to 15 cm depth), all but two of the U.S. biosolids examined would exceed this recommendation when applied [37]. Biosolid application rates on non-agricultural lands (e.g., parks, forests and reclamation sites) may substantially exceed this loading. For example, application of 35 tons per acre was permitted at the Stafford Regional Airport in northern Virginia in 2002. Sludge-associated

APs have been reported to be degraded in a matter of weeks in aerobic soils. However, in soil aggregates entry of oxygen may be impeded and NPs may persist [39]. NPs have been detected in soil cores below the surface for considerable periods after application [40]. The higher ethoxylates and carboxylic acid derivatives would exhibit more mobility due to their greater water solubility. NPs show moderate partitioning to soil, particularly to the organic fraction. Preferential flow via passages in the soil (e.g., insect or animal burrows, shrink/swell fractures . . .) can also enhance migration, as may the presence of natural or synthetic organic matter [5]. The NPs themselves are derived from surfactant parent compounds. Other surfactants, such as linear alkylbenzene sulfonates are also common sludge constituents [5]. NPs have also been detected in groundwater as a result of infiltration from septage drainage fields [41]. In a study of contaminants in secondary treated sewage effluent introduced into a shallow unconfined aquifer near Boston, Massachusetts (USA), NP mobility in the groundwater was significant, but less than more water-soluble organics [42]. However, degradation of the NPs in the groundwater was deemed minimal.

In addition to the APs and PBDEs, we observed the presence of numerous other organic pollutants. Some of them were reported in the NSSS, including polycyclic aromatic hydrocarbons, PCBs, DDT degradation products, and chlor-danes. They were considered singly in the EPA risk assessment process, but additive effects may also be possible. In addition, we observed other organic contaminants in the sludge that were not covered in the EPA risk assessment, including synthetic musk compounds, triclosan and tributyltin (unpublished data). Musks are commonly used as fragrances and some have been found to be bioaccumulative [1]. Triclosan is an anti-bacterial agent, used increasingly in household cleaning products and toothpaste. Tributyltin is a biocide and antifoulant. It has seriously impacted some coastal shellfish populations and is highly toxic to crustaceans. Additional contaminants already detected in WWTP effluents are most certainly present in sludge, including pharmaceuticals, such as ethinylestradiol, the active ingredient in birth control pills.

Improved product stewardship is obviously indicated for biosolids. A recent EPA Inspector General report was highly critical of EPA's oversight of the biosolids program [43]. The concern of the biosolids industry and EPA over organic contaminants also contrasts with that of the composting industry. The latter reacted strongly to reports of the presence of a single herbicide, clopyralid, in U.S. compost [44]. Clopyralid's presence was due to its initial application on lawns and related uses and its subsequent transfer with clippings to compost. While the herbicide has not been reported in sewage sludge, compost derived from waste vegetation may be added to sludge during stabilization. Since its discovery, and observation of associated detrimental effects on plants, individuals in the compost industry have proposed that the manufacturer of clopyralid, Dow AgroSciences, be held accountable for all damages associated with the use of contaminated compost [45]. In the case of biosolids, the

producer/dischargers of the contaminants are essentially anonymous. Precautions such as more extensive re-labeling of clopyralid by Dow to warn applicators that its use precludes subsequent composting of clippings was deemed insufficient to curtail its entry into the compost wastestream. In the case of biosolids, chemicals are intentionally released to the wastestream with no concern regarding their impact on the quality of biosolids and knowledge of the identities of the contaminants therein is incomplete. The composting industry has requested an independent investigation of the extent of clopyralid contamination at composting facilities. EPA has deemed an updated survey of contaminants in biosolids to be unnecessary. Suspension of registration of new clopyralid-containing products and of existing applications in affected geographical areas has been suggested. Consideration of the possible occurrence of herbicide residues in compost as a future requirement for governmental registration of all pesticides has surfaced. In contrast, regulation of the release of many biosolid contaminants, e.g., PBDEs, APs, and pharmaceuticals, to WWTPs is unregulated. Calls have also been made to require Dow to compensate compost facilities and downstream users for real or potential clopyralid-contaminated compost damages, including the cost of land remediation. In the case of biosolids, contamination of land in the United States is expected and is deemed acceptable to "maximum" limits.

Inadequate information on the identities and concentrations of synthetic organic pollutants in sludge has been identified as a major data gap by others, for example, in a 2002 European Union review [46]. Previously, a 1996 National Research Council report questioned EPA's exemption of organic pollutants from the Part 503 sludge rule and indicated that more complete data on the range and concentrations of organic pollutants was essential [47]. The presence of environmentally persistent chemicals, e.g., PBDEs, in land-applied sludge is certainly problematic. However, persistence is a function of ambient conditions. Also, detrimental effects on- or off-site may occur within the lifetime of even short-lived chemicals. Thus, perhaps persistence should not be an essential criterion for a chemical of concern, except in the context of tightly controlled waste land-farming scenarios. Our understanding of the potential detrimental effects of sludge-associated chemicals is limited. Impacts due to multiple interacting chemicals and to an expanded array of potential modes of toxicity, such as endocrine disruption, merit additional investigation. For example, recently sludge extracts have been demonstrated to be estrogenic in *in-vitro* tests [48]. It is now known that current-use organic contaminants of toxicological concern are indeed present at high concentrations in land-applied sludge. Some may be entering through the use of consumer products, not industrial sources. Therefore, more stringent industrial pretreatment regulations may have no effect on releases of them. In conclusion, the above results indicate that the premises utilized by EPA to exempt synthetic organics in land-applied sewage sludge from regulation under Part 503 are questionable.

### AUTHOR'S NOTE

Since submission of this manuscript, the National Research Council, at the request of the US EPA, completed its second review of the technical basis of the biosolids chemical and pathogen regulations [49]. The review concluded that, to date, there was no documented scientific evidence that the Part 503 rule has failed to protect public health. However, it also stated that the applicable epidemiological research conducted has been inadequate. The report also noted the inadequacy of the 1988 NSSS, the need for an updated survey of chemicals in biosolids, as well as to more fully consider exposures and risks associated with the extensive suite of organic chemicals (including PBDEs and NPs) in biosolids.

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